Differential equation of state of a model system with a singular measure: application to granular materials in steady states

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Abstract

A direct modeling of the radial distribution function $g(r)$ for model amorphous system is carried out in terms of generalized functions, without phenomenological parameters and independent of the type of potential. Within the proposed model, physical parameters and details of the considered system contribute through certain homogenous rheological characteristics like for instance compression (compressibility). The combination of this singular model form for $g(r)$ with familiar integral relations yields an Abelian differential form for the equation of state which for a given sample includes a set of relevant material characteristics. These characteristics could be considered as given in every particular case and could be extracted from alternative sources. An appropriate choice of the parameters of the Abelian differential equation gives the possibility of its explicit solution. Obtained results have been analyzed in the context of a model equation of state for driven granular material near the steady states. The relevant functional equations of state which follow from the respective explicit solutions of the Abelian equations are obtained and discussed. © 2002 Published by Elsevier Science B.V.

1. Model for radial distribution function

Intensive study of continuously driven or heated dissipative system shows that inelastic collisions lead to pronounced, long-range forces between the particles [1–3]. Such a model system develops a structure factor that is characteristic of an equilibrium system with a long-range interaction. In particular, molecular dynamic simulations show that

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the dissipative interactions lead to a pair correlation function $g(r)$ that is no longer zero, but becomes close to a certain constant near the origin. [1] The two-particle distribution function $g(r)$ as a probability measure for relative inter-particle configurations could also be defined for such a complex non-equilibrium dynamic dissipative systems, like for instance driven granular materials, but above the steady-state conditions [1–3,5,6]. At present, in spite of numerous successful model approaches (see, for instance Refs. [5–8]), the rigorous kinetic theory of driven granular materials does not exist in closed form like in the case of classical gases or liquids. [2]

The more practical (but, of course, only approximate) way of defining $g(r)$ at present seems to be a direct modeling of their behavior taking into account some main characters known from certain alternative sources (namely, from molecular dynamic simulations, direct physical experiments, or other model approaches).

Along this line, we propose here a simple model expression for $g(r)$, in terms of generalized functions, which include instead of formal phenomenological parameters some additional characteristic namely, compressibility, providing the functional relation between the thermodynamic, structural and other relevant parameters. The choice for a generalized function should not be considered as a challenge to classical statistical mechanics where such a measure like radial distribution function is normally presented only as a weight function for a statistical averaging [4].

We introduce a model radial distribution function constructed in terms of generalized functions

$$g(r) = c + (1 - c)\theta(r - \sigma) + A\delta(r - \sigma),\tag{1}$$

where $\theta(z)$ and $\delta(z)$ are generalized Heaviside (step) and Dirac (delta) functions, respectively, σ is a particle diameter. Clearly, Eq. (1) gives only a sketch for $g(r)$, but the corresponding static structure factor $S(\vec{k})$

$$S(\vec{k}) = 1 + n \int (g(r) - 1)e^{i\vec{k}\vec{r}}\,d\vec{r}\tag{2}$$

calculated with (1) has typical oscillatory and decaying properties known from alternative sources in case of amorphous media [9].

It should be emphasized again that almost all the main relations of statistical physics of amorphous systems are given in terms of integrals of $g(r)$ (but not of $g(r)$ itself).

The value A in form (1) can be extracted, for instance, from the famous relation between the mean energy per particle $\bar{E}$ for a medium of N particles, volume V, pressure P and density $n = N/V$ in equilibrium (at the temperature T), given by

$$\bar{E}\,\frac{\partial n}{\partial p} = 1 + n \int (g(r) - 1)\,d\vec{r}\,.\tag{3}$$

Note, that Eq. (3) does not depend on the inter-particle potential.

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[1] Note, that in classical gases if there were long attractive interactions between the particles $g(r)$ near $r = 0$ is of a power-law form [4].

[2] Where the theory for definition of a full set of the distribution functions of all orders, at least formally exists in the form of BBGKI chains of equations [4].

2. Equation of state

Consider first A is an individual parameter which has a phenomenological nature and which could be extracted from comparison with experimental data for the relevant average values, calculated with the help of $g(r)$ given by Eq. (1). Substituting (1) into (3) (keeping A as a given parameter), after resolving the resulting differential equation for p, we have

$$p = p_0 + \bar{\varepsilon} \ln(1 + X\eta) , \tag{4}$$

where p_0 is a constant of integration, $\eta = nv_0^3$ is a packing fraction(compactivity), $v_0 = \pi\sigma^3/6$, $\tilde{A} = A/\sigma$, $X \equiv 8[c + 3\tilde{A} - 1]$, $\bar{\varepsilon} = \bar{E}/v_0$.

It follows from (4) that within the made assumption the pressure is described by a monotonically (almost logarithmically slowly) increasing function of the packing fraction η for any given value of η.

Problems with practical usage of Eq. (4) follows from the fact that, in general, X is an effective parameter which depends on η (and on $\bar{\varepsilon}$) on their own.

To make the analysis practically more adequate to the requirements of the theory and experiment, one can consider the following approach.

Substituting expression (1) into the preceding Eq. (3) gives the relevant expression for coefficient A in the following form:

$$\tilde{A} \equiv A/\sigma = \frac{1}{24\eta} \left[\bar{\varepsilon} \frac{\partial \eta}{\partial p} - 8(c - 1)\eta - 1 \right] . \tag{5}$$

With Eqs. (1) and (5) we note that the physical properties of considered media contribute to our model through the simplest rheological characteristic represented by the coefficient of compression

$$\frac{1}{n} \frac{\partial n}{\partial p} = -\frac{1}{V} \frac{\partial V}{\partial p} . \tag{6}$$

Under the given temperature T this coefficient is also called isothermal compressibility [4].

Note, for an incompressible non-fluctuating material

$$\frac{1}{n} \frac{\partial n}{\partial p} = 0$$

and

$$\int g(r) \, d\vec{r} = V .$$

Model sketch expression (1) represents some rheological properties of the media through the coefficient of inter-shell particle displacement; damping of correlations through the decay of the static structure factor; and position of their main maximum.

Consider now the expression for the pressure from integral equations theory of equilibrium statistical systems in the following form:

$$p = n\bar{E} - \frac{n^2}{6} \int_0^\infty \frac{dU}{dr} g(r) 4\pi r^3 \, dr , \tag{7}$$

where the function U represents the relevant interparticle potential, which has a bare character.

Substituting the model expression (1) into preceding, and taking into account (5), after some algebra, we obtain the following differential equation for the determination of the pressure p:

$$(p - \alpha_- \eta + \beta \eta^2) \frac{\partial p}{\partial \eta} = -\gamma \eta , \tag{8}$$

where

$$\alpha_{-,+} \equiv \bar{\varepsilon} \pm \frac{\Xi}{24} ,$$

$$\beta \equiv \varLambda + \frac{-c+1}{3} \Xi , \tag{9}$$

$$\gamma \equiv \frac{\Xi}{24} \bar{\varepsilon}$$

and

$$\varLambda \equiv \frac{2\pi}{3} \frac{1}{v_0^2} \left[\int_0^\infty \varphi(r) \, dr + (c-1) \int_0^G \varphi(r) \, dr \right] ,$$

$$\Xi \equiv \frac{2\pi}{3} \frac{\sigma}{v_0^2} \varphi(\sigma) , \tag{10}$$

$$\varphi(r) = r^3 \frac{dU}{dr} .$$

Although Eq. (8) belongs to a class of Abelian differential equations of second kind and in general could not be integrated in quadratures in several particular cases it can be solved explicitly. From now on we refer to Eq. (8) as a differential equation of state. We are going to now show how general Eq. (8) can be solved explicitly in different limits of the packing fraction η.

In spite of the non-integrable (in the sense of there are no possibilities of their integration in quadratures) nature of the general form of Abelian differential equation of second kind (8) we can write down an explicit solution of reduced form for Eq. (8) in the cases, when the value of packing fraction η belongs to certain intervals. Namely, when the third term in Eq. (8) is significantly smaller than the second one

$$\eta \ll \frac{\alpha_-}{\beta} \tag{11}$$

then the reduced equation of type

$$(p - \alpha_- \eta) \frac{\partial p}{\partial \eta} = |\gamma| \eta \tag{12}$$

has the solution [10]

$$p = \alpha_- \eta + \tilde{U} , \tag{13}$$

where function $\tilde{U}$ satisfies the following transcendental equations:

$$\ln(\tilde{U}^2 + \alpha - \eta\tilde{U} + |\gamma|\eta^2) + C - 2\frac{\alpha_-}{\alpha_+}\tanh^{-1}\left(\frac{\alpha_-}{\alpha_+} + \frac{2}{\eta\alpha_+}\tilde{U}\right), \tag{14}$$

or

$$\exp\left(\frac{\eta}{\eta + \tilde{U}}\right) = \frac{C}{\eta + \tilde{U}} \quad \text{when} \quad \bar{\varepsilon} = \frac{|\Xi|}{24}. \tag{15}$$

Here, we take into account that because of $\varphi(\sigma) < 0$, (we consider repulsive potential, which is typical for instance in the case of granular materials if we adopt the existence of not effective, but purely bare type of quasi-stationary potential near the selected steady state), $\Lambda < 0$,

$$\Xi < 0, \quad \gamma < 0 \quad \text{and} \quad q = 4|\gamma| - \alpha_-^2 = -\left(\bar{\varepsilon} - \frac{|\Xi|}{24}\right)^2 \equiv -\alpha_+^2 \leqslant 0,$$

where C is a constant of integration, and Eq. (15) corresponds to the case when

$$\bar{\varepsilon} = \frac{|\Xi|}{24}.$$

In the case, when

$$\eta \gg \frac{\alpha_-}{\beta} \tag{16}$$

an explicit solution of the relevant reduced form of Eq. (8),

$$(p - |\beta|\eta^2)\frac{\partial p}{\partial \eta} = +|\gamma|\eta \tag{17}$$

has the following form [10]:

$$p + c\exp\left(-2\frac{\beta}{|\gamma|}p\right) = \frac{|\gamma|}{2\beta} + \beta\eta^2. \tag{18}$$

Taking the limits $p \gtrless p_0$, where p_0 satisfies to

$$p_0 = C\exp\left(-2\frac{\beta}{|\gamma|}p_0\right) \tag{19}$$

one can write down an appropriate expression for the pressure which follows from Eq. (18)

$$p \approx \begin{cases} \dfrac{|\gamma|}{2\beta} + \beta\eta^2, & p > p_0, \\[2mm] \dfrac{\gamma}{2\beta}\ln\dfrac{c}{\frac{\gamma}{2\beta} + \beta\eta^2}, & p < p_0. \end{cases} \tag{20}$$

Eq. (20) shows that for certain values of the packing fraction η, the model is able to describe also non-monotonic behavior of the pressure under the compaction which is a reminiscent of phase-transition-like ordering. In Fig. 1, the left-hand side of Eq. (18) is plotted against p, showing two different regions of their behavior.

This type of the behavior of pressure known also from equation of state of polyester spheres suspension measures sedimentational equilibrium [8].
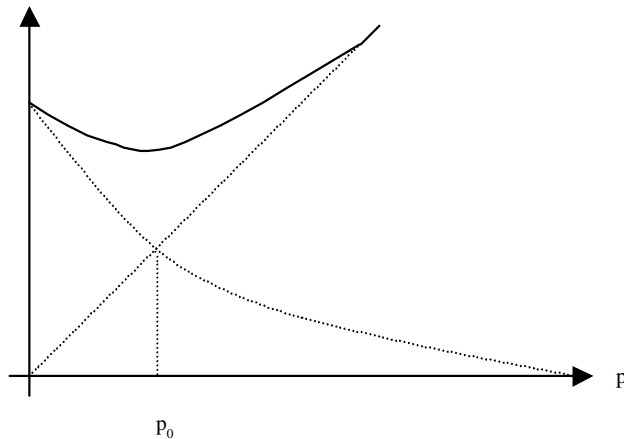
Fig. 1.

3. Driven granular materials in steady state

In this section, we introduce a simple model of driven granular media and to show how the results obtained above can be applied for the construction of a relevant model equation of state which for such a system demonstrates quite non-trivial character. It has been realized that, for any given value of the inelasticity, however small, there is always a size above which the even initially homogenous state loses its stability. The system undergoes a transition towards a state with a shear flow spontaneously developing and possibly towards an inhomogenous clustered state. In order to characterize intrinsic properties like an equation of state, one needs to consider stable homogenous states before any instability occurs. This means, in general, that one has to consider slight inelasticities and finite system sizes where $1/N$ effects (N being the number of grains) are present. In most of the modern approaches to granular materials such systems are described microscopically by means of the inelastic hard sphere (IHS) model. Grains are modeled as soft–hard spheres that dissipate energy at collision through a constant restitution coefficient e. It is quite remarkable that such a simple model can already account for many peculiarities of the observed behavior [5–8]. Also, it is clear that it is necessary to inject energy into the system in order to keep it stationary.

Note that there have been many attempts to describe the average properties of dissipative systems (see, for instance, Refs. [1–3,5–8]). However, the full statistical mechanics of IHS system, including the theory of their correlation functions, analogos to that for simple liquids, remains a problem for further research.

Here, to develop the application of the model described in the preceding sections, we consider our system in (and in the vicinity) of a s.c. non-equilibrium steady state where the energy losses due to inelasticity and energy input compensate each other providing thermalization of entire system and where all macroscopic quantities (including, of course, the pressure) are stationary(quasistationary) and can be averaged.
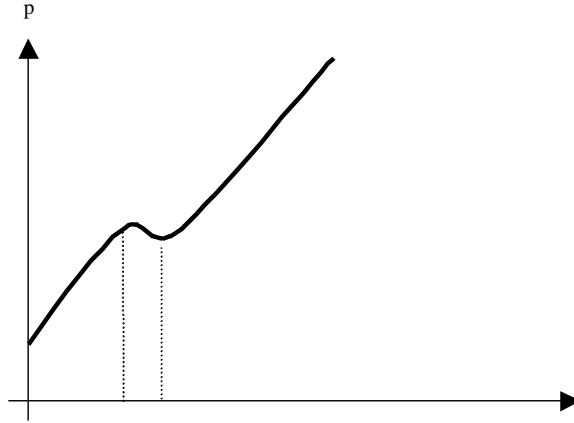
Fig. 2.

Note that generally as in granular media there is no equivalent to a free energy or an entropy, the pressure cannot be defined thermodynamically but only mechanically (with the help of a virial expression, for instance). From that point of view, by "equation of state" one could understand also the relation between the energy input rate, the number of particles (grains), the system size and the kinetic energy of the particles in the steady state [11].

In order to write down the pressure as an ensemble average we will consider the behavior in the steady state (and in a small vicinity of it) the model of driven granular material which is constructed as follows. The system of IHS is heated volumetrically (to avoid the phenomenon of inelastic collapse). The IHS collides inelastically with a coefficient of restitution e. During each collision, an amount of energy

$$\frac{\mu}{2}(1-e^2)\gamma^2 \,,$$

where μ is the reduced mass and γ is a relative velocity of the colliding particles, is dissipated. Thus, the rate of energy input in the steady state is

$$Q = \frac{\mu}{2}(1-e^2)\gamma^2 \,. \tag{21}$$

The relevant analogs of the molecular energy $k_B T$ in the steady state of considered model for dissipative system is their kinetic temperature (energy) ε

$$\varepsilon \equiv \frac{\eta}{2}\upsilon^2 = \frac{Q}{1-e^2} \,. \tag{22}$$

Naturally, in the limit of elastic spheres e should be put equal to unity. Adopting from now the kinetic isomorphism between ε from Eq. (22) and $\bar{\varepsilon}$ from Eq. (3), we want to focus now on no waver the pressure p, the isotropic part of the stress in a hard sphere system, introducing the rheological parameters in our model permitting us to describe also a critical phenomenon like order–disorder transitions. It is intuitively clear that in the limit of high densities, the cage effect, where particles are captured by their

neighbors becomes important and the system could even change from the disordered to the ordered state. Although here free-volume theory can be formulated, to propose an approach that is valid for both intermediate and low- and high-densities is still a difficult problem [8].

We emphasize that model equation of state described in the previous section which represents all densities compression rate limits and thus has a global character. Namely, combining the results represented by Eq. (18) and (22) and then plotting schematically p against the packing fraction η (see Fig. 2), we observe that the pressure of our model system increases with the density, except for an intermediate range of packing fraction η, where a disorder–order phase transitions can be expected to occur.

4. Discussion and conclusions

In this paper we propose a simple model of the radial distribution function $g(r)$ in terms of generalized functions (and this we call singular measure for our system). We take such a step for the definition of statistical measure because not $g(r)$ itself, but its average will be considered in our analysis. In this way we achieved the simplicity in the calculations of relevant averages and the possibility to insert into the model self-consistently the rheological characteristics instead of extra phenomenological parameters. This last step is particularly important in the case when these parameters could not be simply controlled like for instance in the case of non-equilibrium dissipative systems and driven granular materials, in particular. Another non-trivial character of the model lies in the fact that combining the singular measure with familiar integral relations, for instance, for the pressure yields an equation of state in the form of an Abelian differential equation which for certain intervals of values of the packing fraction reduce to forms which can be integrated explicitly. The obtained general expressions are then analyzed with respect to driven granular materials in the vicinity of their steady state, where energy losses due to inelastic collisions between the particles and energy input by volumetric heating compensate each other (because of the adoption that energy is going directly to every individual particle, the phenomenon of inelastic collapse which typically exists due to dissipation is avoid). In the considered model the pressure is shown to increase with the packing fraction (density), except for a certain intermediate range, where discontinuity takes place and where one can expect structural transitions like disorder–order to occur. Above this certain values of packing fraction (namely, low packing) the sample is clondy: "fluid". Below (higher packing) material coal exhibits partial ordering. The model therefore show more rich scenario of behavior then a simple power-law dependence of pressure against density. Note that a familiar expression of the pressure in the form of the square polynomials

$$p = A\eta + B\eta^2 \tag{23}$$

satisfies the equation of state in the form of Eq. (8) under the certain values of their coefficients, but represents only a monotonic behavior.

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